# I. DIENE ADDITION PRODUCTS TO DIAROYLETHYLENES AND THEIR TRANSFORMATION PRODUCTS

# II. A STUDY OF THE PRODUCTS FROM *CANNABIS SATIVA*

BY

RICHARD BENJAMIN WEARN

B.S., Clemson College, 1937

M.S., University of Illinois, 1939

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1941

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# I. DIENE ADDITION PRODUCTS TO DIAROYLETHYLENES AND THEIR TRANSFORMATION PRODUCTS

## Introduction

In a recently published article[1], Adams and Gold showed that butadiene, 2,3-dimethylbutadiene, and cyclopentadiene added quantitatively to dibenzoylethylene to form dibenzoylcyclohexenes. Syntheses from these adducts were developed for the corresponding dibromo derivatives, dihydroisobenzofurans, *o*-dibenzoylbenzenes, oxido-tetrahydronaphthalenes, and substituted naphthalic anhydrides. Similar reactions have also been carried out on the adduct of dibenzoylethylene and 1,4-dimethylbutadiene by Adams and Geissman[2].

In this work it was planned to test the generality of these synthetic methods when dibenzoylethylene was replaced by various substituted dibenzoylethylenes.

## Experimental and Discussion

*Trans*-di-*p*-chlorobenzoylethylene and *trans*-di-*p*-toluylethylene were added quantitatively to butadiene and to 2,3-dimethylbutadiene to form the corresponding diaroylcyclohexenes. Both these products and their dibromo derivatives were dehydrated to the dihydroisobenzofurans and dibromotetrahydroisobenzofurans respectively. By treatment with bromine and sodium acetate in acetic acid, the dihydroisobenzofurans were converted into *o*-diaroylbenzenes. The corresponding isobenzofurans were prepared by reduction of the *o*-diaroylbenzenes with zinc dust and alkali. Maleic anhydride was condensed with the isobenzofurans to form oxido-tetrahydronaphthalenes. These products were dehydrated with hydrogen chloride in methanol to the corresponding naphthalic anhydrides.

Cyclopentadiene added in good yield to di-*p*-chlorobenzoyl-, di-p-toluyl-, and dimesitoyl- ethylenes. These adducts could not be closed to form furans.

Dimesitoylethylene added to butadiene, but not to 2,3-dimethylbutadiene. The butadiene adduct could not be closed to the furan.

### Bibliography

1. Adams and Gold, J. Am. Chem. Soc. *62*, 56 (1940).
2. Adams and Geissman, ibid., *61*, 2083 (1939).

## II. A STUDY OF THE PRODUCTS FROM *CANNABIS SATIVA*

### Introduction

In cooperation with the United States Bureau of Narcotics, a study of the chemistry of the drug marihuana is under way in the Illinois laboratories. The active principle of this drug, derived from the hemp plant *Cannabis sativa L.*, has been found to be concentrated in a high boiling red oil. In this laboratory it is obtained by fractional distillation *in vacuo* of the alcoholic extract from the plant.[1] Investigation of this oil led to the isolation of a new compound, cannabidiol; and also of cannabinol, which had previously been isolated by European workers.[2] In this laboratory, the structure of cannabinol has been shown by synthesis to be 1-hydroxy-3-*n*-amyl-6, 6, 9-trimethyl-6-dibenzopyran. Tetrahydrocannabidiol has been shown to be 2-(3′-menthyl)-5-amylresorcinol, and cannabidiol is the same except that there are four less hydrogen atoms in the menthyl residue. Cannabinol and cannabidiol are physiologically inactive, but cannibidiol has been isomerized under mild conditions to $\alpha$ or $\beta$ tetrahydrocannabinol, a substance which has a potent marihuana activity. This work, as well as most of that carried out in this thesis, has been published recently.[3] This thesis involves experimental work on the synthesis of cannabinol, attempts to locate the double bonds in

cannabidiol, and investigations of certain fractions obtained in the distillation of crude red oil.

## Experimental and Discussion

A study of the amount of cannabidiol in the extracts of the *Cannabis sativa* hemp plant from Minnesota and from Danville, Illinois and of the resin, Indian *Charas*, was made. Cannabinol was isolated as the 3,5-dinitrophenylurethane from Indian *Charas*.

Olivetol was prepared by the method of Suter and Weston.[4]

1-*n*-Amyl-3,5-cyclohexanedione was synthesized in the following manner: *n*-hexaldehyde and acetone were condensed to form hexylidene acetone. The product was reacted with malonic ester in the presence of sodium ethylate. The intermediate compound cyclized and, upon hydrolysis, was converted into the final product. This compound was identical with the product formed by reduction of olivetol by Baker[5] and used by him in the synthesis of cannabinol.

Cannabidiol dimethyl ether failed to condense with maleic anhydride.

Cannabidiol was isomerized in the presence of *p*-toluenesulfonic acid in benzene according to the procedure of Adams and McPhee[6] to give tetrahydrocannabinol, a compound having a potent marihuana activity.

Both $\alpha$ and $\beta$ tetrahydrocannabinols were converted into the methyl ethers.

As a result of the ozonization experiments on cannabidiol dimethyl ether, formaldehyde (as its methone derivative), *n*-caproic acid (as its *p*-bromophenacyl ester), and the 2,4-dinitrophenylhydrazone of a new compound, $C_{14}H_{20}O_3$ (postulated to be 2,6-dimethoxy-4-*n*-amylbenzaldehyde), have been isolated.

A sesquiterpene, to be called "cannabinene," has been isolated from the steam distillates from hemp plant extract. The molecular refraction value and the presence of two double

bonds (quantitative hydrogenation) show it to be dicyclic. Ozonization produced formaldehyde and a high boiling, neutral methyl ketone which oxidized easily to an acidic methyl ketone.

Palmitic acid was isolated from the low boiling fraction from crude red oil.

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3. Adams, Baker, Cain, Clark, Hunt, Loewe, Pease, Wearn, and Wolff, J. Am. Chem Soc. *62,* 196, 732, 735, 1770, 2194, 2197, 2201, 2204, 2208, 2215, 2245, 2401, 2402, 2405, 2566. (1940).
4. Suter and Weston, ibid *61,* 232 (1939).
5. Adams, Baker, and Wearn, ibid *62,* 2204 (1940).
6. Adams and McPhee, to be published.

## VITA

The writer was born August 1, 1916, in Newberry, South Carolina. He attended the public schools in that city and graduated from Newberry High School in June, 1933. His undergraduate training was obtained at Clemson College, where he received the degree of Bachelor of Science in June, 1937. From that time until September, 1938, he was employed as chemist with National Starch Products, Inc., in New York City. In the fall of 1938, he entered the Graduate School of the University of Illinois, where he has continued his studies for the past three years. In 1939, he received the degree of Master of Science. He served as a teaching assistant during the year 1939-1940 and held the Dow Chemical Company Fellowship during the year 1940-1941. He is a member of Phi Kappa Phi, Phi Lambda Upsilon, and Sigma Xi.

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